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Preparation of Si-microspikes by Electrochemical Etching and Field Emission Characteristics from Diamond particles on the Si-microspikes prepared by Plasma CVD

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Sharp needle-like Si-microspikes array was prepared on Si surface electrochemically by anodization. Tops of Si-microspikes were covered with diamond particles by plasma chemical vapor deposition with CH_4 /H_2 gas.
Field emission characteristics from the Si-microspikes, and from diamond particles on Si flat surfaces and on the Si-microspikes were clarified. The diamond particles on the Si-microspikes gave the lowest threshold voltage for the field emission among them.

Key words: Si, microspikes, diamond, field emission

シリコンマイクロスパイクの電気化学的エッチングによる作製とプラズマ CVD で作製されたマイクロスパイク上のダイヤモンドからの電界電子放出特性

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シリコン表面を電気化学的に陽極酸化することによって，鋭い針状のシリコンマイクロスパイク列を作製した。このシリコンマイクロスパイクの先端にメタン・水素混合ガスを用いたプラズマ CVD 法でダイヤモンド粒子を形成した。
シリコンマイクロスパイク、平坦シリコン基板に形成したダイヤモンド及びシリコンマイクロスパイクの先端に載せたダイヤモンドからの電界電子放出特性を明らかにした。
これらの試料においてマイクロスパイク上のダイヤモンドが最も低い閾電圧を示した。

キーワード: シリコン、マイクロスパイク、ダイヤモンド、電界放出

1. Introduction

Since the first report of micropore formation in anodized p-type Si by Propst and Khol[1], many reports have been reported on the control of micropores formation on Si and their applications for various devices such as photo-emission and field electron emission devices[2][3][4]. We have also studied micropores on Si depending on the detailed preparation condition and succeeded to control the shape of the pores edge by selective etching and removal of pore walls. Indeed we obtained arrays of needles of Si by this method, with which preliminary measurements of field emission characteristics have also been carried out.

On the other hand, carbons have also attracted much attention as field emission device. For example, diamonds are considered to have surface of negative electron affinity which may enhance the field emission. Carbon nano-tubes are also known as the candidate of field emission device[5][6][7][8]. We have also reported that electron emission from the sharp wall edges of carbon inverse opals can be also excellent emission sites[9].

From these back ground, in this paper, we carried out detailed study of the surface micropores formation, resulting in the formation of Si microspikes array. Then we prepared carbons such as diamonds on these Si devices. The field emission characteristics from the Si-microspikes, and from diamond particles on Si flat surfaces and on the Si-microspikes have been measured and compared.

2. Experimental

2.1 Experimental procedure of micropores and microspikes formation

The starting material was the p-type Si wafer with (100) surface, whose back surface was mechanically ground and then coated with successively deposited Ti/Ni/Au. The anodic reaction was carried out at room temperature using a sample holder, in which the Au-plated Cu block was pressed to the back surface of the sample by a spring used for the electrical contact and the front surface of the sample was covered by a Teflon plug with a window through which the anodic reaction occurred.

The electrolyte was 48wt.% HF : de-ionized water : isopropyl alcohol(IPA)=1:1:6 (vol.). Anodization was carried out for 30 min, changing the current density from 0.5 to 63 mA/cm^2 and the anodized surface morphology was investigated by Scanning Electron Microscope (SEM).

We expected that the beams at corners of rectangular parallel-piped pores might be modified to field emission arrays by a selective removal of pore walls. For such a purpose, an anisotropic wet etching was carried out to pores by using the etching solution of 1 mol KOH : IPA=4.8 : 1 (vol.) at 50℃.

The typical etched surfaces observed by SEM is shown in Fig.1. As evident in this figure, sharp Si microspikes were formed by these procedures.

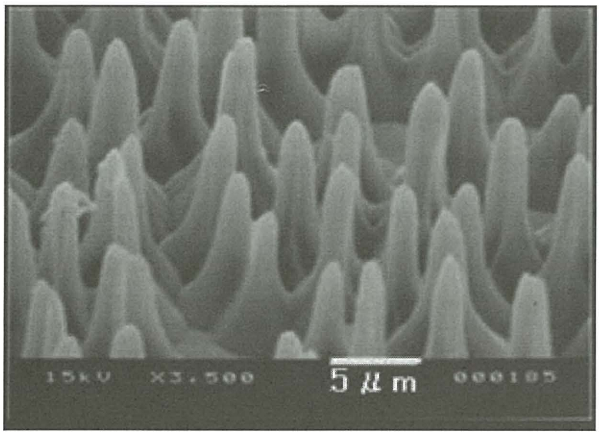


Fig.1: SEM image of a typical etched surface of Si by anodization.

図 1. 典型的な陽極酸化によるエッチングで処理された Si 表面の電子顕微鏡写真

2.2 Diamond growth

Diamond particles were formed on various Si(100) substrates at 500°C under the discharge of H_2 and CH_4 mixture gas with H_2 : CH_4 ratio of 99：1 at 120 Torr for 60, 120,180 and 300 minutes under an applied voltage pulse of 500V (150 μs ON and 50μs OFF) and current of 1 A.

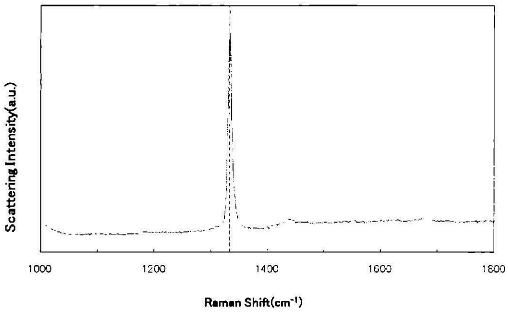


Fig.2: Raman spectrum of a diamond particle grown on Si for 60 min.

図 2. Si 上に 60 分間成長したダイヤモンドのラマンスペクトル

Growth of diamond prepared with a growth time of 60 min. was confirmed by the observation of a peak at 1333cm^{-1} in a Raman spectrum as shown in Fig.2, where the Raman spectra were taken in the backscattering geometry using a 514.5 nm Ar-ion laser for the excitation. A SEM image of the diamond particles on Si substrates for the deposition time of 60 min is shown in Fig.3.

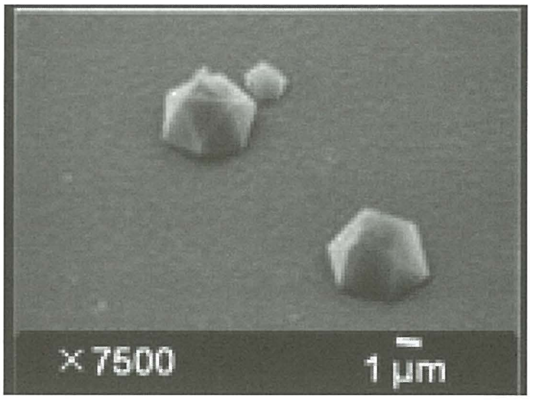


Fig.3: SEM image of the diamond particles on a Si substrate for the deposition time of 60 min.

図 3. Si 表面上に 60 分間堆積したダイヤモンド粒子の走査電子顕微鏡写真

Figure 4 shows typical SEM images of diamond particles on the Si microspikes

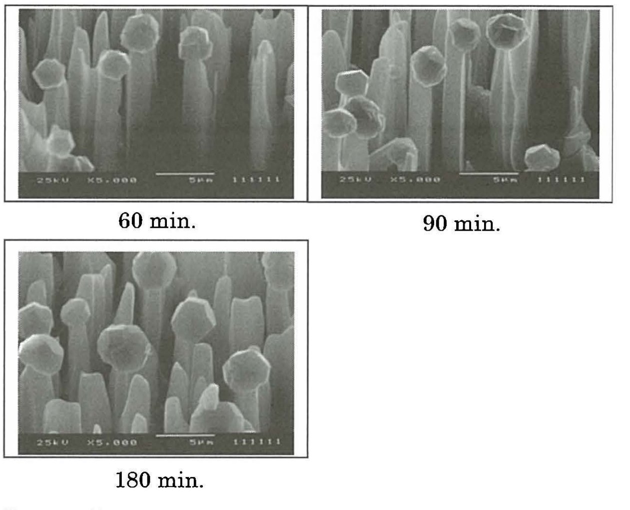


Fig.4: SEM images of the diamond particles on Si microspikes for various deposition times.

図 4. 種々の堆積時間における Si マイクロスパイク上のダイヤモンド粒子の走査電子顕微鏡写真

electrochemically formed. The particles were formed on some of tip tops of Si and not all the tip tops were capped with the diamond particles.

2.3 Field emission measurements

The field emission measurements were performed for the samples as an emitter in a high vacuum chamber (about 10^{-7} Torr). We used a tungsten probe with a diameter of 500 μm as an anode. The cross-sectional area of the anode was 1.96 x 10^{-7} m^2. The field emission current density – electric field characteristics were studied for various distances (z) between the anode and the specimen.

3. Results and discussion

Field electron emission current was not observed from the flat Si substrate. However, upon anodization of the Si substrate, micropore formation progresses and then sharp Si micospikes have been formed. From these Si-microspikes clear field emission current was observed as shown in Fig.5.

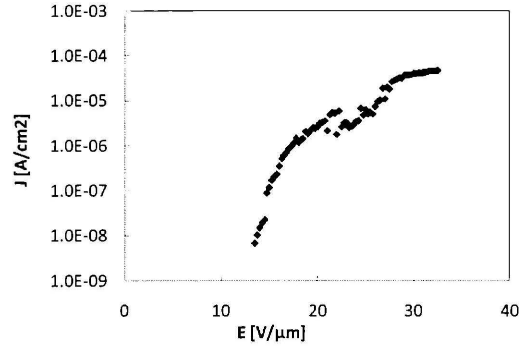


Fig.5: Voltage dependence of field emission current from Si microspikes.

図 5. Si マイクロスパイクからの電界放出電流の電圧依存性

The emission should be induced by the field enhancement at the tip of the Si spikes.

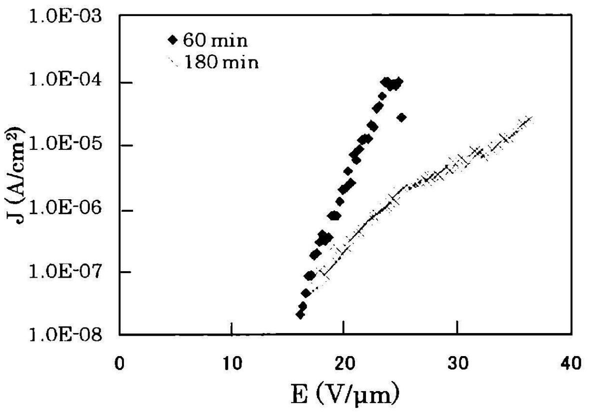


Fig.6: Voltage dependences of field emission current from diamond particles grown on the flat Si surface for the deposition time of 60 min and 180 min

図 6. Si 平坦表面上に堆積したダイヤモンド粒子からの電界放出電流の電圧依存性

◆：堆積時間 0 分, ×：180 分

To clarify the effect of diamond deposition for the field emission, the field emission characteristics were studied in the flat Si substrate with the deposited diamond particles on it. As evident in Fig.6, in the flat Si substrate with the diamond particles deposited on it, clear field emission current was observed. This may be explained by both the enhancement of electric field at the corner edge of the diamond particles as evident in Fig.3 and also the electron affinity characteristic of diamond. In this case of diamond formation by plasma deposition method with the discharge of H_2 and CH_4 mixture gas, the surface of the diamond particles may be terminated with hydrogen. It is known that saturated hydrocarbons are considered to have negative electron affinity.

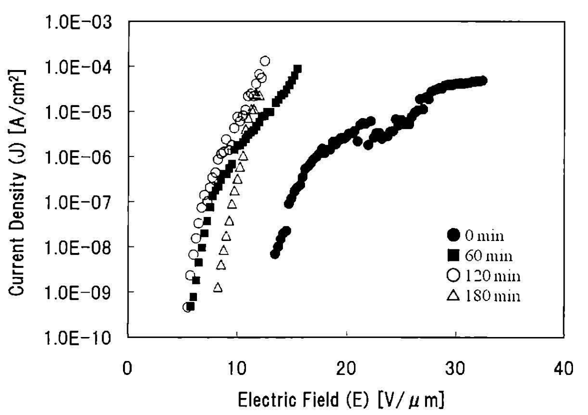


Fig.7: Voltage dependences of field emission current from Si microspikes deposited with diamond particles on it at various deposition times.

図 7. ダイヤモンド粒子を種々の時間堆積したSi マイクロスパイクからの電界放出電流の電圧依存性

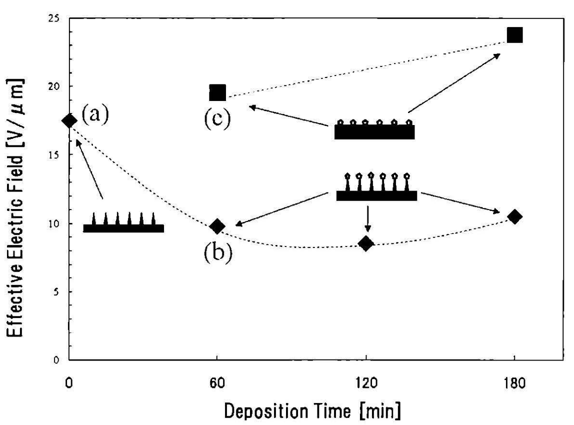


Fig.8: Dependence of the threshold electric field for the field emission from (a) the Si microspikes, (b) diamond particles on the microspikes and (c) diamond particles on the flat Si surface upon the deposition time of diamond particles.

図 8. Si マイクロスパイク(a)及び Si マイクロスパイク上に堆積したダイヤモンド粒子(b)，並びに平坦 Si 上に堆積したダイヤモンド粒子(c)，からの電界放出電流の閾電界の堆積時間依存性

It should be noticed, as also evident in Fig.7, that in the diamond deposited Si micospikes, the emission current was remarkably enhanced at low voltage and the threshold field was much suppressed. However, it should be mentioned that longer time deposition of diamond does not induce further reduction of the threshold field of the field emission current as also evident in this figure and clearly shown in Fig.8, where threshold fields are summarized in the three cases.

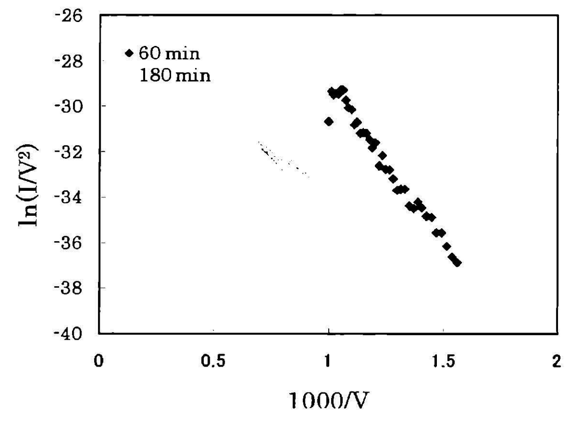
Figure 9 shows Fowler-Nordheim plots, that is, the field emission current density J – electric field E characteristics in Si-microspikes, Si-flat substrate with diamond particles on it, and Si-micorospikes with diamond particle caps.

The threshold electric field of the field emission from the Si micro-tips was decreased remarkably upon diamond particle deposition These J-E characteristics seem to be saturated in current density range of J > 10^{-3} – 10^{-5} (A/cm^2).

These J-E characteristics were analyzed by the Fowler-Nordheim (FN) equation for the field emission. The emission current density J as a function of the local electric field at the emitter surface F is given by

$J=(AF^2/\phi)\exp(-B\phi^{3/2}/F)$ (A/m^2) with A=1.56 x 10^{-10} (AV^{-2}), B=6.83 x 10^9 (V eV$^{-3/2}$m^{-1}) and ϕ as the work function.

As evident in Fig.9, in the FN plots for the observed current-voltage characteristics, data points in a low-voltage range of the FN plots were approximately on a straight line, which indicates that the analysis of the data



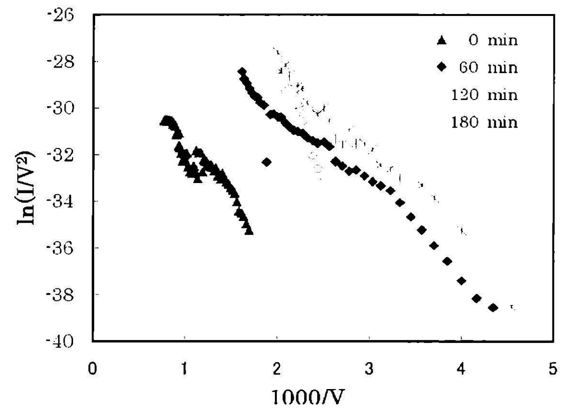


Fig.9: Fowler-Nordheim plots of field emission current-voltage characteristics shown in Figs.5, 6 and 7.

図9. 図5, 6, 7の電界放出電流の電圧依存性のファウラー・ノルドハイムプロット

utilizing FN equation is reasonable.

Judging from the Fig.4, the sharpness of the emission site seems not so much changing with diamond deposition.

We are also expecting the increase of the emission stability, because diamond should be more stable than Si tips during emission.

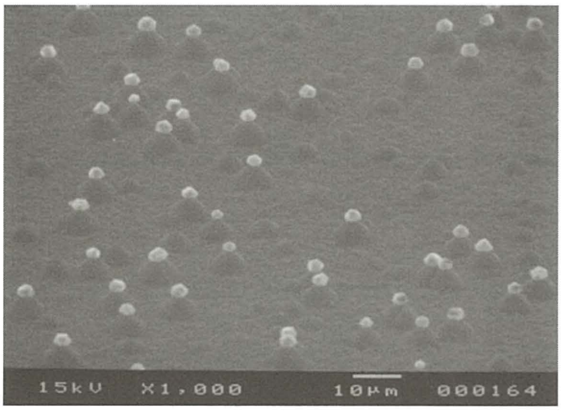


Fig.10: SEM image of the Si surface formed by anisotropic electrochemical etching after the deposition of diamond particles on the flat Si surface.

図10. 平坦Si表面にダイヤモンド粒子を堆積後異方性エッチングで形成した表面の走査電子顕微鏡写真

For the preparation of Si microspikes fully capped with diamond particles, anisotropic electrochemical etching was performed to Si flat substrates deposited with diamond particles on it. As evident in Fig. 10, with progress of electrochemical etching Si-micorotips all capped with diamond particles were obtained. The emission characteristics of these samples are now under study.

4. Summary

Sharp Si-microspikes array was prepared on Si surface electrochemically by anodization. Tops of Si-microspikes were covered with diamond particles by plasma chemical vapor deposition with CH_4 /H_2 gas.

Field emission characteristics from the Si-microspikes, and from diamond particles on

Si flat surfaces and on the Si-microspikes were clarified. The enhancement of the field emission current upon deposition of the diamond particles grown on the Si microspikes has been clearly observed.

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